Magnetostatics #2

Paramagnetism

- Seldom is there the spherically symmetric distribution of charge in solids that creates zero built-in magnetic moment and just a small diamagnetic response.
- Usually, there is a built-in magnetic moment. Two types are prevalent:
  (1) orbital dipole: $\vec{m}_l$, and (2) spin dipole: $\vec{m}_s$
- Atoms with net orbital or spin angular momentum can have large paramagnetic effect. (e.g. atoms with partially filled inner shells: transition elements and rare earths).
  Best example is atoms with an odd number of electrons so one spin is unpaired
  Fundamental unit for magnetic dipoles is the Bohr magneton = magnetic moment for ground state of hydrogen.

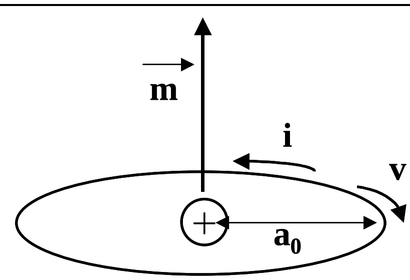


Fig. 1.

$$\vec{m}_B = i\cdot\vec{A} = \frac{e\upsilon}{2\pi a_0}\cdot\pi a_0^2\cdot\vec{A} \qquad\qquad i\cdot\vec{A} = ea_0\vec{\upsilon}/2$$

But for Bohr *quantization* rules:

$$m\upsilon\cdot r = L = n\hbar \qquad \text{n = 1, 2, 3, …}$$

So for ground state, $m\upsilon r = m\upsilon a_0 = \hbar$ and

$$m_B = i\cdot A = eva_0/2 = \frac{e\hbar}{2m} \equiv \mu_B = 0.93\times10^{-23}\,A-m^2 \ .$$

So for built-in magnetic dipoles, we write

$$\vec{\boldsymbol{m}} = -g\mu_B\vec{\boldsymbol{J}}, \quad \vec{\boldsymbol{J}} = \vec{\boldsymbol{L}} + \vec{\boldsymbol{S}}$$

Note: minus sign because m defined in terms of current, L in terms of electron motion

g $\rightarrow$ gyromagnetic ratio ≈ 2 for electron spin; ≈ 1 for orbital angular momentum.

$Potential\ energy = -\vec{m}\cdot\vec{B}_{local} = g\mu_B\vec{J}\cdot\vec{B}_{local} = m_j g\mu_B B_{local}$. That is, for J pointed anywhere in the upper hemisphere (polar axis defined by direction of B_{local}), the potential energy is positive. And for J pointed anywhere in the lower hemisphere, the potential energy is negative.

For a single spin, $m_j = \pm\frac{1}{2}$, g = 2 (e.g. single electron) , $|\vec{\boldsymbol{m}}| = \mu_B$

Hence, $U_{PE} = \pm\mu_B \cdot B_{local}$, the + sign meaning that the spin is pointed along the $\vec{B}$ axis. For spin ½, we have two possible energy values, $U_1 = -\mu_B B$ $U_2 = \mu_B B$. These are conveniently represented by the energy diagram to the right:

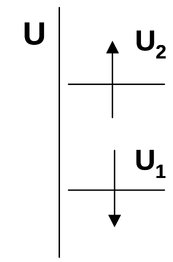


Fig. 2.

Since spins are hidden variables within atoms and atoms are generally distinguishable, we can apply the *Maxwell-Boltzmann* statistics: probability of magnetic moment being aligned along B: $p_1 = \frac{e^{-U_1/k_BT}}{e^{-U_1/k_BT} + e^{-U_2/k_BT}}$. $= \frac{e^{\mu_B B/k_BT}}{e^{\mu_B B/k_BT} + e^{-\mu_B B/k_BT}}$

and $p_2 = \frac{e^{-\mu_B B/kT}}{e^{\mu_B B/kT} + e^{-\mu_B B/kT}}$

Thus, the mean magnetic dipole is: $\langle\vec{m}\rangle = p_1\vec{m}_1 + p_2\vec{m}_2 = \mu_B(p_1 - p_2)\hat{z}$

$$<\vec{m}> = \frac{(\mu_B e^{\mu_B B/k_BT} - \mu_B e^{-\mu_B B/k_BT})}{e^{\mu_B B/k_BT} + e^{-\mu_B B/k_BT}}\cdot\hat{z}$$

$$= (\mu_B \tanh \mu_B B/k_BT)\cdot\hat{z}$$

Simple picture of two possible energy states (Fig. 3):

High energy state: $U = -\vec{m}\cdot\vec{B} = \mu_B B$

Low energy state: $U = -\vec{m}\cdot\vec{B} = -\mu_B B$

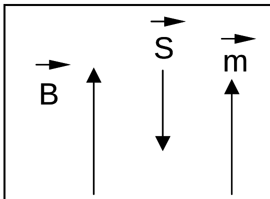


Fig. 3

High-temperature limit: $\mu_B B/k_B T << 1$:

$$|<\vec{m}>| \approx \frac{\mu_B[2\mu_B B/k_B T]}{2} \approx \mu_B{}^2 B/k_B T \;:$$

$$\alpha_m = \frac{|<\vec{m}>|}{B} = \mu_B{}^2/k_B T$$

$$\chi_m = \frac{n\alpha_m\mu_0}{1-n\alpha_m b\mu_0} \approx \frac{n\mu_B{}^2\mu_0}{k_B T} \equiv \frac{C}{T}$$; Curie Law, C → Curie constant

For more general total angular momentum J, and according to quantum mechanics, m_j has 2J+1 equally spaced levels:

$$U = -\vec{m}\cdot\vec{B} = g\mu_B\vec{J}\cdot\vec{B} = m_j g\mu_B B$$

For example: if the total angular momentum quantum number γ = 3/2, m_j = -3/2, -1/2, ½, and 3/2, so that

$$<\vec{m}> = \frac{\sum_j^{2J+1} \vec{m}_j e^{-U_j/k_B T}}{\sum_j^{2J+1} e^{-U_j/k_B T}} = \frac{\sum_j^{2J+1} g\mu_B m_j e^{m_j\mu_B B/k_B T}}{\sum_j^{2J+1} e^{m_j\mu_B B/k_B T}}\hat{z}$$

It can be shown that this becomes:

$$|<\vec{m}>| = g\cdot\gamma\cdot\mu_B B_J(x)\,.$$

where B_J is called the Brillouin function and g is the Lande g factor, and

$$x = g\gamma\mu_B B/k_B T$$

$$B_J(x) \equiv \frac{2J+1}{2J}\coth\left[\frac{(2J+1)x}{2J}\right] - \frac{1}{J}\coth(\frac{x}{2J})$$

$$<\vec{M}> = n<\vec{m}> = ngJ\mu_B B_J(x)\cdot\hat{z}$$

$$\alpha_m \equiv \frac{gJ\mu_B B_J(x)}{B_{local}}$$

In high-temperature limit we use the Taylor expansion coth(x) ≈ 1/x to get

$$\chi_m \approx n\alpha_m\mu_0 \approx \frac{nJ(J+1)g^2\mu_B{}^2\mu_0}{3k_BT} \equiv \frac{np^2\mu_B{}^2\mu_0}{3k_BT} = \frac{C}{T}$$

$$p = g\sqrt{J(J+1)}$$

$$C \rightarrow \text{Curie constant } = \frac{np^2\mu_B{}^2\mu_0}{3k_B}$$

In an advanced course on Quantum Mechanics it can be shown:

$$g = 1 + \frac{\gamma(\gamma+1) + s(s+1) - \beta(\beta+1)}{2\gamma(\gamma+1)}$$

Example: atom with single unpaired spin

$$\chi_m = n\mu_B{}^2\mu_0/k_BT \qquad \mu_B = 0.93\times10^{-23}\,A-m^2 \qquad n \square\, 5\times10^{28}/m^3,\ T = 300K$$

$$\Rightarrow \chi_m \approx 1.31\times10^{-3}\ @300K$$

This is substantially stronger in magnitude than the diamagnetic for such an atom !

For partially filled inner shell atoms (e.g. transition elements), the $|\vec{J}|$ is large and χ_m tends to be even larger, up to values of ~5x10^{-3}.

Ferromagnetism

We derived the relation for the *ferroelectric effect* from relationships between microscopic and macroscopic fields. This also works for ferromagnetic materials

$$\vec{M} = \frac{n\alpha_m\vec{\mathrm{B}}_{\mathrm{in}}}{1 - n\alpha_m b\mu_0} \qquad\qquad \frac{1}{3} \le b \le 1$$

$\Rightarrow$ expect ferromagnetism when $n\alpha_m b\mu_0 \approx 1$

Take, for example, spin system where $\vec{M} = n\vec{m} \approx n\alpha_m \vec{B}_{local} = n{\mu_B}^2 / k_B T$. So,

$$\alpha_m = {\mu_B}^2 / k_B T$$

And ferromagnetic condition is:

$$\frac{n{\mu_B}^2 \mu_0 b}{k_B T} \geq 1 \qquad \text{or} \qquad n \geq k_B T / b{\mu_B}^2 \mu_0$$

So at T = 300 K: $n > 0.38 \times 10^{32} / b$

Recall b has max value of 1.0 in classical magnetostatics:

So the minimum value is $n > 3.8 \times 10^{31} / m^3$; $(3.8 \times 10^{25} / cm^3)$. Clearly this is much larger than occurs commonly in solids.

So Pierre Weiss theorized (and *Heisenberg* proved) that there is a big contribution to b from spins. This can be quantified by:

$$\vec{\boldsymbol{B}}_{local} = \vec{\boldsymbol{B}}_{in} + \mu_0 b \vec{\boldsymbol{M}}$$

with the possibility that $b >> 1$.

Take, for example, Nickel, fcc lattice a = 3.52 Å

$$n = \frac{4}{(3.52)^3} = 0.092 \times 10^{30} = 9.2 \times 10^{28} / m^3$$

So, $b > 0.38 \times 10^{32} / 9.2 \times 10^{28} = 413$ to satisfy ferromagnetic condition.

Simple Model for Ferromagnetism

Recall temperature dependent M for spin 1/2 system:

$$\langle M \rangle = n\mu_B \tanh \mu_B B_{local} / k_B T \quad \text{(paramagnetic)}$$

But *ferromagnetic* spontaneous response requires:

$$\vec{\boldsymbol{B}}_{local} = \mu_0 \vec{\boldsymbol{M}} d \text{ even when } B_0 = 0$$

$$\vec{\boldsymbol{B}}_{local} / \mu_0 = \vec{\boldsymbol{M}} d, \; d > 0$$

$$(\vec{B}_{in} = \vec{B}_0 - N\mu_0\vec{M} = -N\mu_0\vec{M};\ \vec{B}_{local} = \vec{B}_{in} + b\mu_0\vec{M} = \vec{M}(-N\mu_0 + b\mu_0) \equiv d\mu_0\vec{M}$$

So we have: $$\langle M \rangle = n\mu_B \tanh(\frac{\mu_0\mu_B d\cdot M}{k_B T})$$

This is an implicit equation in M so can be solved by plotting the left and right sides separately and then looking for intersections.

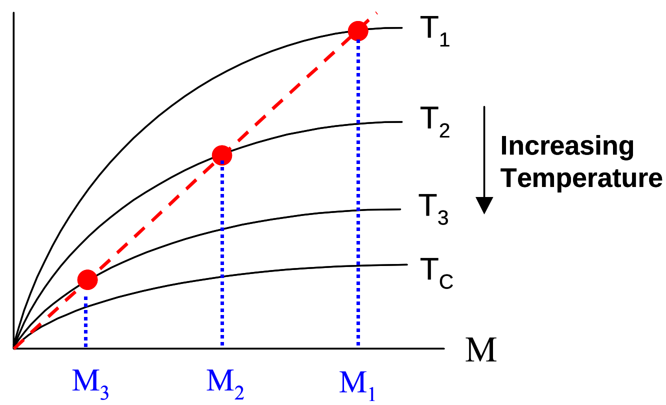
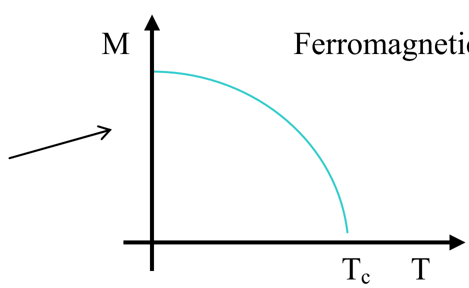


Fig. 4.

As expected: $M_1(T_1) > M_2(T_2) > M_3(T_3)$ for $T_1 < T_2 < T_3$

And eventually the intersection point goes to $T = T_C$ where $M \to 0$.

The full curve looks as shown below:



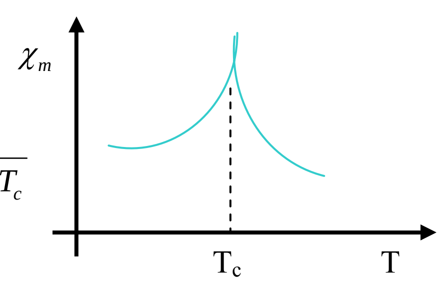
Ferromagnetic → Paramagnetic phase

2nd-order phase transition

often well fit by:

$$M = M_s(1 - T/T_c)^n$$

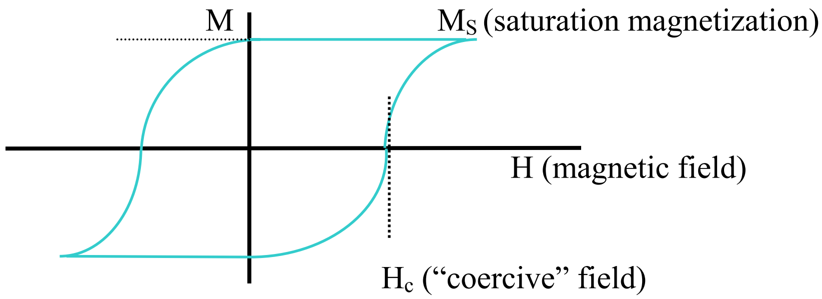
As in *ferroelectrics*, susceptibilities often are singular



Often well fit by: $\chi = \frac{C}{T - T_c}$

Ferromagnetic elements	**T_C**
Fe	1043
Co	1388
Ni	627
Gd	292
Dy	88

And as with ferroelectrics, all ferromagnetic solids display a hysteresis loop.



As in *ferroelectrics*, the spontaneous polarization is so strong that it takes significant external B (or H) to overcome it. So all *ferromagnets* show saturation.

Figure of merit is energy density:

From *thermodynamics* $dU_m = \mu_0 \vec{H} \cdot d(\vec{M}V)$

$$U'_m \approx \mu_0 H_C M_S \text{ if B is uniform}$$

So for Alnico-V (an alloy of: 51% Fe, 8% Al, 14% Ni, 24% Co, 3% Cu):

$\mu_o H_C$ –> coercivity ~0.1 T [MKSA; recall 10^4 Gauss = 1 T]

$\mu_o M_S$ –> saturation ~ 1.25 W/m^2 = 1.25 T . So,

$$U'_m \cong \mu_0 H_C M_S \approx (0.1/\mu_0)(1.25) \approx \frac{0.125}{\mu_0}\frac{J}{m^3} \approx 0.1 \text{ J/cm}^3$$

Alnico V:	51% Fe	8% Al	14% Ni
	24% Co	3% Cu	

Other strong *ferromagnets* are rare-earth cobalt and iron-oxide alloys (e.g. $SmCo_5$, $FeOFe_2O_3$). In the past couple of decades, there has been a generation of even stronger magnets, the so-called "super magnets" made from an alloy of iron, neodymium, and boron.